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Optical properties of three-dimensional P(St-MAA) photonic crystals on polyester fabrics

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ABSTRACT

The three-dimensional (3D) photonic crystals with face-centered cubic (fcc) structure was fabricated on polyester fabrics, a kind of soft textile materials quite different from the conventional solid substrates, by gravitational sedimentation self-assembly of monodisperse P(St-MAA) colloidal microspheres. The optical properties of structural colors on polyester fabrics were investigated and the position of photonic band gap was characterized. The results showed that the color-tuning ways of the structural colors from photonic crystals were in accordance with Bragg's law and could be modulated by the size of P(St-MAA) colloidal microspheres and the viewing angles. The $L^*a^*b^*$ values of the structural colors generated from the assembled polyester fabrics were in agreement with their reflectance spectra. The photonic band gap position of photonic crystals on polyester fabrics could be consistently confirmed by reflectance and transmittance spectra.

1. Introduction

Different from the traditional coloration principles using dyes or pigments, structural color mostly arises from selectively reflected light by a special physical periodically-textured structure interacting with incident light, such as dispersion, scattering, interference and diffraction [1], and can be produced via numerous microscopic nanostructures. Photonic crystals [2–5], the materials in which a periodic spatial modulation in the refractive index leads to coherent scattering of light and alters the propagation modes of light of wavelengths commensurate with the length scale of the periodicity, have been a very active area. Particularly, the structural color properties of three-dimensional photonic crystal structure depended on the 'photonic band gap' have attracted much interest from researchers. The 'photonic band gap' is a range of frequencies where light is forbidden to exist within the bulk of the photonic crystals, and is determined by the crystal lattice and period [6,7]. If the photonic band gap falls into the visible light range between 380 nm and 780 nm, the visible light of specific wavelengths are not allowed to propagate in the photonic crystal structure, thus being selectively reflected. Then the structural colors would be produced on the surface of periodic photonic crystals.

Polymers play an important role in the development of photonic materials. These materials offer several advantages such as low cost, low processing temperature, and safety [8]. The self-assembly of polymer microspheres is widely used to fabricate photonic crystals, which also can be named as colloidal crystals [9]. Colloidal crystals can be prepared by self-assembly using many different techniques, including gravitational sedimentation [10,11], vertical deposition [12,13], electrophoretic deposition [14], microfluidic cell method [15] and so on, among which gravitational sedimentation, well-known to create colloidal crystals of spherical colloids with well-defined shape and controllable crystal structure, is thought of as the simplest and most convenient method to construct photonic crystal structure [10].

In recent years, the typical properties of structural colors by photonic crystals have fostered a great number of potential applications: inkless printing, reflective flat display, gas sensing, paints, photonic papers and cosmetics [16–18]. Especially, the common self-assembly procedure to fabricate photonic crystals is drying a colloidal suspension on a solid substrate [19], such as glass, silicon and silicon nitride, which has been well developed. However, the research related to self-assembly of photonic crystals and its structural colors on textile were rarely reported. In textile industry, the main way to color textile is attaching colorants of dyes or pigments onto fibers, yarns and fabrics on dyeing and printing processes. When the dyes or pigments encounter light, they absorb some wavelengths of light and reflect the rest into our eyes [20]. Much

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to our delight, the fabrication of the structural colors of photonic crystals on textile materials has aroused some interest due to its potential to initiate a new coloring mode in dyeing and finishing process. However, the textiles have rougher and more fluctuant surfaces than the common solid substrates and there are many gaps among fibers and yarns in textiles, which make the fabrication of photonic crystals on textiles more difficult than on solid substrates.

Compared to the colors produced by conventional dyeing and printing processes, structural colors exhibit high brightness, high saturation, less discoloration and iridescent effect, i.e., color changes with the viewing angle due to Bragg diffraction from the lattice planes [9,21]. It is believed that the optical properties of photonic crystals can directly determine the quality of the resulting structural colors. Therefore, it is significative to study the optical properties of photonic crystals on the textiles.

It is thought that the photonic crystals suppress propagation of light in specific directions and wavelength ranges, which forms the basis of optical properties of structural colors. The structural colors of the photonic crystals with face-centered cubic (fcc) structure can be expressed by Bragg's equation with Snell's law as [22,23]:

$$\lambda_{\max} = \frac{2d_{hkl}}{m}\left(n_{\text{eff}}^2 - \sin^2\theta\right)^{1/2} \tag{1}$$

where $\lambda_{\max}$ is the wavelength of the reflectance peak maximum (i.e. the position of the photonic band gap), d_{hkl} is the interplanar spacing between hkl planes, m is the order of the Bragg diffraction, n_{eff} is the effective refractive index of the photonic structure and θ is the angle between the incident light and the surface normal of the sample (same as viewing angle).

For the fcc lattice, the interplanar spacing d_{hkl} is given by [22]:

$$d_{hkl} = \frac{\sqrt{2}d}{\sqrt{h^2+k^2+l^2}} \tag{2}$$

where d is the size of polymer colloidal microspheres. Therefore, d_{111} is defined as $\sqrt{2/3}d$.

The effective refractive index is expressed as [23]:

$$n_{\text{neff}}^2 = n_p^2 v_p^2 + n_m^2 v_m^2 = 0.74n_p^2 + 0.26n_m^2 \tag{3}$$

Here, n_p and n_m are refractive indices of the colloidal microspheres and the surrounding medium, respectively; V_p and V_m the are volume fractions of the colloidal microspheres and surrounding medium. According to Waterhouse and Waterland [23], the V_p and V_m are approximately 74% and 26%, respectively.

Therefore, on the basis of Bragg's equation with Snell's law, the photonic crystals on textiles exhibit structural colors that can be modified by changing a number of factors, including the diffracting plane spacing, the Bragg glancing angle and the refractive indice of the photonic crystal array. Although the optical properties of photonic crystals on solid substrates have been well known, the relative research on soft substrates such as textile has rarely been reported.

In our previous paper, we have prepared a series of P(St-MAA) colloidal microspheres with high degree of sphericity, controllable size and narrowed size distribution by means of soap-free emulsion copolymerization and proposed to construct high-quality photonic crystals on polyester fabrics as a new coloration strategy to produce structural colors [25]. In this paper, we elaborated on the different tactics to tune structural colors of photonic crystals on polyester fabrics, and investigated the photonic band gap position by reflectance and transmittance spectra. To create structural colors on textiles is a challenging task, but remains to be extremely important in practice. It is believed that the vivid structural colors of three-dimensional (3D) photonic crystals on textiles will revolutionize the textile and fashion industries in sight.

2. Experimental

2.1. Materials

Styrene (St, A.R. grade, Yongda Reagent Factory, Tianjin, China) and methacrylic acid (MAA, A.R. grade, Kemiou Chemical Reagent Factory, Tianjin, China) were purified by distillation under reduced pressure. Ammonium persulfate (APS, A.R. grade, Yongda Reagent Factory, Tianjin, China) was used without further purification. Nitrogen (98%, Jingong Specialty Gases Co., Ltd., Hangzhou, China) was used as received from laboratory. Black and white plain weave polyester fabrics of same texture were bought from the local market. Deionized water with a resistivity of 18.0 MΩ cm was obtained from a Millipore-Q Plus water purifier and used throughout the experiments.

2.2. Synthesis of monodisperse P(St-MAA) microspheres

The monodisperse P(St-MAA) microspheres were prepared by soap-free emulsion copolymerization with St and MAA as comonomers and APS as an initiator [24,25]. The size of the P(St-MAA) microspheres produced in this method is highly dependent on the different concentrations of St, MAA and APS, and the basic properties of resultant P(St-MAA) microspheres is presented in Table 1. Syntheses were carried out in a 500 ml four-necked round-bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, thermometer and a mechanical stirrer. With one of sample E as an example, the procedure used was outlined as below. 20 g St, 3 g MAA and 195 g H_2O were added to the four-necked round-bottom flask. Nitrogen gas was then slowly bubbled through the resulting two-phase system and the mixture commenced to be mechanically stirred vigorously. When the mixture was heated to 70 °C, 0.1 g APS dissolved in 5 g H_2O was introduced into the reactor. The reaction mixture was maintained at 70 °C for 8 h. The whole reaction was carried out in nitrogen atmosphere with mechanical stirring at around 350 rpm. The resulting colloidal suspensions of P(St-MAA) microspheres were then filtered through a glass wool (a plug about half the size of a penny) to remove any large agglomerates and then stored in sealed PET plastic bottles at room temperature for later use without other purification. Note that in order to avoid the deposition of colloidal microspheres, it is necessary to carry out the subsequent self-assembly process on polyester fabrics as soon as possible. When the parameters of the polymerization were changed, different diameters of P(St-MAA) microspheres can be prepared, it can refer to our previous article [25].

2.3. Fabrication of structural color on polyester fabrics

The photonic crystals with structural colors were fabricated by allowing a dilute colloidal suspension of P(St-MAA) to deposit on

Table 1
The basic properties of resultant P(St-MAA) microspheres.

Sample	Solid content (wt%)[a]	Average diameter, Z_D (nm)[b]	Particle dispersion index (PDI)[b]
A	10.91	304	0.013
B	9.22	286	0.013
C	9.99	270	0.01
D	10.55	255	0.033
E	10.37	234	0.03
F	10.85	222	0.025
G	10.38	207	0.023
H	10.32	185	0.068

[a] Solid content (wt%) referred to the proportion of solid material in P(St-MAA) emulsion.
[b] Determined by a Malvern laser particle sizes analyzer.